Highly photosensitive helium diluted amorphous silicon 1.5 eV band gap: Role of pressure

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Highly photosensitive low band gap ($\geqslant 1.5$ eV) hydrogenated amorphous silicon (a-Si:H) films have been developed by plasma enhanced chemical vapor deposition using helium dilution of the process gas, silane at substrate temperature 210 °C. Low band gap of a-Si:H films is achieved by reducing bonded hydrogen content and hence by increasing compactness of the films. At the optical gap ~ 1.5 eV, a-Si:H film has high mobility lifetime product, $\eta\mu\tau$ (8×10^{-5} cm^{-2} V^{-1}) and photosensitivity ($>7\times 10^4$) values. The defect density of the material is as low as 7.8×10^{15} cm^{-3} eV^{-1} and hydrogen content is 4.54 at. %. Low band gap amorphous silicon germanium (a-SiGe:H) films reported so far do not have such high $\eta\mu\tau$ and photosensitivity values at 1.5 eV optical gap. Thus, this low band gap a-Si:H films can be used as intrinsic layer in the bottom cell of a multijunction solar cell replacing a-SiGe:H alloy films. © *1995 American Institute of Physics.*

Low band gap amorphous silicon germanium alloy in a multijunction solar cell serves an important role to enhance its efficiency[1] and stability under prolonged illumination.[2] Consequently, at the present stage of amorphous silicon solar cell technology, development of high-quality low band gap alloys is an important task. However, it has been generally observed that the optoelectronic properties deteriorate gradually with the decrease of optical gap from 1.7 eV accompanied by the increase of defect density. Moreover, the deposition condition which produces high-quality a-SiGe:H material suffers from the drawback of low growth rate.[3–5] As an alternative approach, low band gap amorphous silicon (a-Si:H) has been developed under high substrate temperature (T_s>400 °C),[6] hot wire method and also by chemical annealing technique (T_s>300 °C).[7] However, the usual fabrication temperature of p-i-n solar cell with glass substrates is nearly 200 °C. For T_s>200 °C, transparent conducting oxide (TCO) (first layer of TCO/p-i-n-metal cell) degrades under plasma.[8] Thus, the low band gap a-Si:H so far prepared under high T_s could not be used in solar cell. In this communication, the development of low band gap (1.5 eV) amorphous silicon at 210 °C temperature is reported for the first time. In this regard helium dilution of silane under high chamber pressure has been used. The results are interpreted in terms of the growth kinetics of films under helium dilution.

All the samples for this study have been prepared by radio frequency powered (13.56 MHz) plasma enhanced chemical vapor deposition technique details of which has been reported elsewhere.[5] During film deposition substrate temperature and rf power density have been kept at 210 °C and 15 mW/cm^2, respectively while chamber pressure has been varied from 0.5 to 2.0 Torr. For all the films, 94% helium dilution has been used while total flow rate of silane and helium was 42.5 sccm. Optical measurement has been done by UV-VIS spectrophotometer. The hydrogen bonding configuration has been analyzed by fourier transform of infrared spectroscopy and bonding hydrogen content has been calculated from the wagging vibrational mode at 630 cm^{-1}.[9,10] The midgap defect density has been determined by

electron spin resonance technique and valence band tail width called Urbach energy has been estimated from the slope of absorption spectra (absorption co-efficient versus energy) obtained from constant photocurrent method. Photoconductivity was measured under 50 mW/cm^2 white light from a tungsten halogen lamp. During mobility lifetime product ($\eta\mu\tau$) measurement, the monochromatic light of wavelength corresponding to absorption co-efficient (α)$\sim 10^3$ cm^{-1} of the materials was chosen. All the $\eta\mu\tau$ measurement were done under same electron hole pair generation rate 3×10^{18} cm^{-3} s^{-1}.

Figure 1 shows the variation of deposition rate (R_D), optical gap (E_{opt}), and bonded hydrogen content (C_H) of amorphous silicon with chamber pressure (P_r). It may be observed from the figure that as P_r increases from 1.0 to 2.0 Torr R_D increases sharply with P_r. This sharp increase of R_D is an indication of the change of plasma energy transfer mechanism during film growth. In the same figure it is seen that E_{opt} decreases monotonically from 1.68 to 1.50 eV with the increase of P_r up to 1.8 Torr. However, E_{opt} increases once again for P_r>1.8 Torr. The trend of C_H versus P_r curve is same as E_{opt} versus P_r. The optical gap of the films have been calculated from Tauc's formula.[11] Tauc's plot has been shown in Fig. 2. Figure 3 represents stretching vibrational mode[10,12] of amorphous silicon films deposited under different chamber pressures. It may be observed that with the increase of pressure infrared absorption around both peaks at 2010 and 2100 cm^{-1} (which correspond to Si-H and SiH$_2$/SiH$_2)_n$, respectively reduce monotonically. However with the increase of pressure from 1.8 to 2.0 Torr absorptions due to both type of bonds increase. The corresponding change of atomic percentage of bonded atomic hydrogen content (C_H) with the chamber pressure are shown in Fig. 1.

Figure 4 has displayed the variations of mobility lifetime product ($\eta\mu\tau$), darkconductivity (σ_D), and photosensitivity (σ_{Ph}/σ_D) with the chamber pressure, where σ_{Ph} is photoconductivity under white light. It may be observed from the figure that $\eta\mu\tau$ value is maximum, i.e., 10^{-4} cm^{-2} V^{-1} for $P_r\sim 1.4$ Torr. The darkconductivity increases and photosensitivity decreases as P_r increases from 1.0 Torr and both
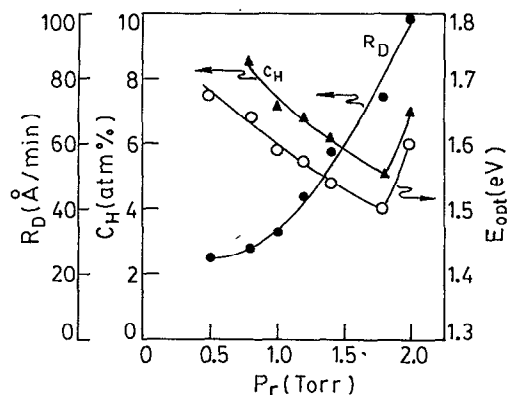
FIG. 1. Variation of deposition rate, R_D, optical gap, E_{opt}, and bonded hydrogen content, C_H of amorphous silicon with chamber pressure.
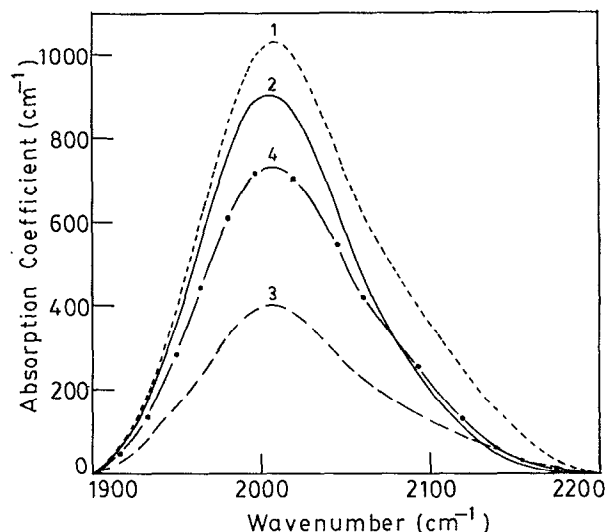

FIG. 3. Stretching vibrational spectra of amorphous silicon prepared under different chamber pressure. Curves, 1, 2, 3, and 4 correspond to the films deposited under 0.5, 1.4, 1.8, and 2.0 Torr, respectively.

curves saturate finally. It may be recalled from Fig. 1 that the optical gap of amorphous silicon prepared under 1.8 Torr pressure is 1.5 eV. Figure 4 shows that this film has high mobility lifetime product ($>8 \times 10^{-5}$ cm^{-2} V^{-1}) and high photosensitivity ($>7 \times 10^4$). Amorphous silicon-germanium (a-SiGe:H) films reported so far do not have such high $\eta \mu \tau$ and σ_{Ph}/σ_D values at 1.5 eV optical gap. The midgap defect density (N_s) and Urbach energy (E_0) are given in Table I. The value of N_s is low throughout the band gap region. At 1.5 eV it is lower by at least one order of magnitude compared to that of a-SiGe:H alloy of same band gap.

From the experimental observation it may be noted that low band gap amorphous silicon films have been produced by reducing bonded hydrogen content (C_H) within the film. This reduction of C_H may be explained from the growth kinetics of the films. Hydrogen elimination from solid phase, during thin film formation is always associated with supply of lots of energy.[13] This is evident from the facts that so far, low hydrogen content ($C_H < 5$ at %) has been developed at high substrate temperature ($T_s > 400$ °C), by hot wire method or by chemical annealing along with high T_s (>300 °C). Generally device quality a-Si:H films has been prepared un-

der low rf power and pressure (α-regime).[14] With the increase of power or pressure, energy gaining mechanism of electrons changes and its energy steadily increases (γ-regime).[14] In α-regime the energy of electrons are low and these low-energy electrons oscillate collisionlessly in weak rf field (bulk plasma). However, with the increase of pressure (P_r) collision frequency between electrons and neutral species increases thereby allowing electrons to gain energy from the expansion of sheath. In other words, the peak of electron energy distribution function shifts towards higher energy with the increase of P_r.[15] These highly energetic electrons excite diluent helium atoms to their metastable (20 eV) and ionization level (24 eV)[16] instead of producing ionic species (as in case of high rf power). Moreover, with the increase of chamber pressure the probability of ionization of excited helium (He*) increases due to metastable atom-metastable atom collision.[17] On de-excitation of these metastable and ionic helium, lots of electronic energy is trans-
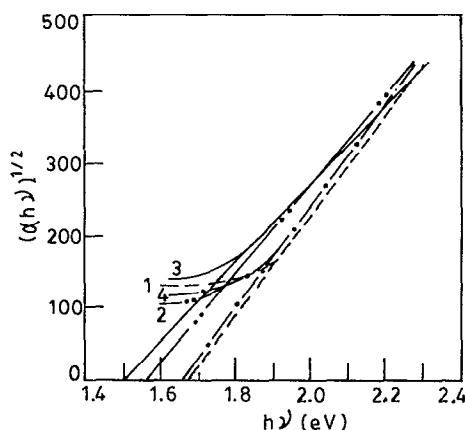

FIG. 2. Tauc's plots at different chamber pressure. Curves 1, 2, 3, and 4 correspond to the films deposited under 0.5, 1.2, 1.8, and 2.0 Torr, respectively.
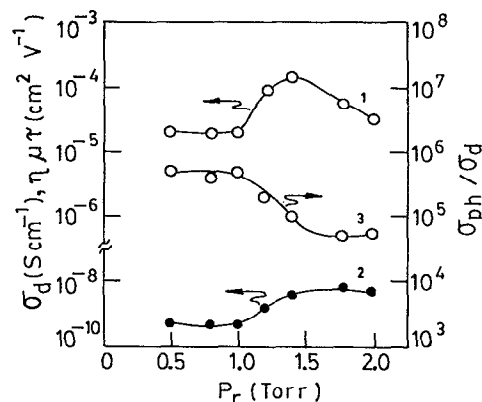

FIG. 4. Variations of mobility life-time product, $\eta \mu \tau$ (O), darkconductivity, σ_D (●), and photosensitivity, σ_{Ph}/σ_D (O) with chamber pressure.

TABLE I. Defect density and Urbach energies of a-Si:H films having different optical gaps.

Chamber pressure (Torr)	Optical gap (eV)	Defect density (10^{15} cm^{-3} eV^{-1})	Urbach energy (meV)
0.5	1.68	9.0	51
1.2	1.57	7.5	52
1.8	1.51	7.8	54
2.0	1.60	9.0	59

ferred to the growing surface as well as to the reacting species which enhances their mobility. This excess energy increases the effective temperature of the surface. All these factors accelerate structural relaxation and thus compact network structure with low hydrogen content is formed. With the further increase of pressure, electron energy increases so much that it initiates secondary electron emission from the electrodes. This unwanted process helps powder formation within the plasma and thereby film properties deteriorate.

In conclusion, we have developed for the first time a low band gap ($\sim$1.5 eV) amorphous silicon thin film with high photoconductivity, high mobility-lifetime product, and good photosensitivity at 210 °C substrate temperature. This has been achieved in practice by reducing bonded hydrogen content and by increasing compactness of the film. The preparation temperature of the film (210 °C) is compatible for the fabrication of solar cells. Thus, this low band gap a-Si:H film can be successfully used in the bottom cell of a multijunction solar cell.

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J. Appl. Phys., Vol. 78, No. 1, 1 July 1995

Hazra, Middya, and Ray   583